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An investigation into the effect of fast heating on fluidity development and coke quality for blends of coal and biomass

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ABSTRACT

The addition of biomass to coking coals can reduce operational costs and carbon emissions but also reduces fluidity development. The use of heating rates up to 20 °C min^{-1} in the softening stage of coal has been investigated using high-temperature small-amplitude oscillatory-shear (SAOS) rheometry to improve the fluid characteristics of binary blends of two coking coals with Scots pine. The effects of biomass concentration and particle size, biomass torrefaction, pellet mass and thermal pre-treatment of the blend on fluidity development and semicoke strength have also been studied. Fluidity increased with an increase in heating rate and an increase in the final temperature for fast heating. Relationships were found between the minimum complex viscosity of the blend, the heating rate and the concentration of biomass, which have been used to propose an equation to calculate the heating rate necessary to achieve optimum fluidity for a particular blend with biomass. The fluid characteristics of the blend were not affected to a great extent by the particle sizes of the biomass studied (<500 μm and >500 μm) or the torrefaction of the biomass (250 °C for 1 h in N_2), were increased by an increase in pellet mass, and were destroyed by blend pre-heating. The semicoke strength of the blend with a mass fraction of 10% Scots pine and fast heating (10 °C min^{-1}) proved to be higher than that of the coal alone with slow heating (3 °C min^{-1}) and resulted in a 3% reduction in non-renewable carbon emissions.

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1. Introduction

The use of biomass as additive in coking blends offers the advantages of reducing production costs by replacing expensive prime coking coals and also reducing non-renewable carbon emissions into the atmosphere as biomass is carbon neutral. This neutrality is based on the assumption that the carbon released by biomass is re-captured from the atmosphere during photosynthesis. Most of the research to date on blends of coal and biomass has focused on the characterization of the pyrolysis behaviour of coal and biomass blends through thermal gravimetric analysis to elucidate possible synergistic effects [1–4]. This research has found contradictory findings regarding the degree of interaction between the components, which have been attributed to differences in pyrolysis conditions (e.g. reaction system, sample

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mass, heating rate) or sample characteristics. However, there is little research related to the effects of biomass addition to coking blends in terms of fluidity development and coke strength during carbonization. Some studies have found that the fluidity of the coking blend [5,6] and the coke strength [7,8] are usually reduced by the addition of biomass. However, there are several factors that can be varied to improve fluidity development and coke strength. Some of these factors include the heating rate during carbonization and the particle size of the biomass.

It is well known that an increase in heating rate is accompanied by an increase in the amount of fluid material in coal whilst the plastic zone extends towards higher temperatures as indicated by Gieseler plastometry [9,10]. This has also been observed through high-temperature rheometry [11] by showing a decrease in the minimum complex viscosity (i.e. increase in fluidity) and a shift in the temperature of maximum fluidity to higher temperatures as the heating rate increases. Thus, fast heating rates could potentially be used in blends of coal with biomass to achieve similar fluid characteristics that the coal alone under typical heating conditions in coke ovens during carbonization (i.e. 3–5 °C min^{-1}). Indeed, blends with biomass have been proven to possess similar fluid characteristics that prime coking coals as long as the heating regime is increased significantly from 3 °C min^{-1} to 180 °C min^{-1} just before coal softening [6]. However, these fast heating rates are not feasible for commercial application and further investigation is required to ascertain whether lower, more realistic heating regimes can still improve the fluid characteristics of the blend.

On the other hand, the effect of biomass particle size on fluidity and coke strength has also been studied in woody biomass and charcoal. Lower particle sizes for charcoal have been reported to cause a higher reduction in fluidity [10,12]. MacPhee et al. [8] found a sharp drop in coke strength with charcoal additions of 2–10% to coal blends, but an increase in the particle size of charcoal had a dramatic improvement on the quality of the coke produced with 5–10% additions. Similarly, Ota et al. [13] found that the reduction in coke strength caused by a waste wood was inhibited by an increase in particle size. These findings might suggest that coke strength could be compromised by low cohesion between coal and biomass. In this manner, Matsumura et al. [7] proposed that it is necessary to decrease the contact area between woody biomasses and coke in order to increase the addition of biomass without lowering coke strength. These authors identified the low bulk density and collectability of the biomass as the main drawbacks in their use as additives in coking blends, and they proposed that compressive forming at 200 °C could effectively decrease the contact area by increasing both particle size and density.

There is another problem associated with biomass in coking blends, namely its high volatile matter content that will cause a reduction in coke yield. This drawback could be partially solved either by identifying biomass samples that produce high carbon yields during pyrolysis or by pre-treating the biomass sample. For instance, Diez et al. [5] studied *Eucalyptus* wood, its components xylan, cellulose and lignin, and the charcoal and tars obtained during carbonization, and found that charcoal and lignin possess the lowest conversion yield at the thermoplastic temperature range of coal (350–500 °C), and therefore, will produce the highest coke yield. Another way of reducing the conversion yield of the biomass and increasing its bulk density is by means of mild pyrolysis or torrefaction, which is a thermochemical process involving the slow heating of biomass to temperatures in the range 200–300 °C in the absence of oxygen [14]. The torrefied biomass is characterised by higher fixed carbon and atomic carbon, and the H/C and O/C atomic ratios resemble those of low rank coals [15,16]. Since the most reactive lignocellulosic component is hemicellulose, the composition of the biomass will have an effect on the amount of solid residue after torrefaction [15].

The present work expands on a previous study [6], which investigated the effect of different biomass on fluidity development in coking blends using high-temperature SAOS rheometry. The study found that up to 5% by weight of sugar beet can be added to coking coals without altering its viscoelastic properties, while the addition of pine wood or miscanthus had a negative effect on fluidity development which could be countered by fast heating to the softening temperature of the coal (i.e., 180 °C min^{-1} instead of 3 °C min^{-1}). The present work focuses on the determination of the optimum heating conditions in pellets of blends of coal with biomass in order to achieve optimum fluid characteristics without impairing semicoke strength. The effects of biomass particle size, biomass torrefaction, pellet mass and blend pre-heating on fluidity development have also been studied.

2. Materials and methods

2.1. Materials

This work was performed on two coals and wood substrates of unknown provenance, for which the chains of custody are not known. While the authors believe that this work exemplifies the difference between coals and the particle sizes of the biomass, there is a reasonable concern that there may be substrate factors that influence the general applicability of the results obtained. The characteristics of the coals used in this study, namely coals A and B, are presented in Table 1.

Scots pine (*Pinus sylvestris*) was supplied by BP and the proximate analysis is presented in Table 2.

Two particle size fractions of Scots pine were studied (<500 μm and >500 μm), and the biomass was also torrefied under nitrogen to increase its density and char yield. The <500 μm fraction was characterised by spherical particles whereas the >500 μm fraction was characterised by stick-like shapes of up to 0.5 mm in diameter and 3 mm in length. During torrefaction, the biomass was heated from 50 °C to 250 °C at 3 °C min^{-1} in nitrogen and thereafter the temperature was held at 250 °C for 1 h.

2.2. Methods

Small-amplitude oscillatory shear (SAOS) rheometry measurements were carried in a Rheometrics RDA-III high-torque controlled-strain rheometer. A detailed description of the analysis conditions can be found in the work carried out by

Table 1 – Characteristics of the coals.

	Coal A	Coal B
VM (% daf)	31.9	25.5
Ash (% db)	9.8	10.1
C (% db)	78.6	79.1
H (%)	4.8	4.4
N (%)	0.9	0.7
S (%)	0.3	0.2
O[a] (%)	15.4	15.6
Mean vitrinite reflectance	1.05	1.21
Vitrinite (%)	76.0	59.0
Inertinite (%)	13.0	32.4
CSR	50	65
CRI	30	26
I_{40}	52	48
I_{10}	24	24
FSI	7.5	6.5
Gieseler max. fluidity (ddpm)	534	48
Temperature max. fluidity (°C)	447	459
Dilatation (%)	88	4

a By difference.

Castro Díaz et al. [6]. The complex viscosity (η^*) and change in plate gap (ΔL) were recorded throughout the test. The tests involved different heating regimes to elucidate the effect on fluidity development.

Standard or slow heating tests consisted of heating the sample at 3 °C min^{-1} from either room temperature (biomass) or from 330 °C (coals and blends). For the coals and blends, the heating rate between room temperature and 330 °C was approximately 180 °C min^{-1} because there were not significant differences in the rheological properties of coal A in the thermoplastic temperature range (350–500 °C) when starting the slow heating stage (i.e. 3 °C min^{-1}) at 50 °C or at 330 °C. The fast heating regimes used in the rheometer can be grouped into two:

1) Tests to optimise the heating rate. The samples were heated from room temperature to 330 °C at 180 °C min^{-1} (1st stage) followed by fast heating to a temperature (T_i) in the softening temperature range (2nd stage) and then slow heating of 3 °C min^{-1} to 500 °C (3rd stage). In these tests, the faster heating rate in the second stage was either 6 °C min^{-1}, 10 °C min^{-1} or 20 °C min^{-1}.
2) Tests to optimise the temperature at which slow heating starts (T_i). The tests were similar to those described above but the fast heating rate was kept constant and T_i was changed by increments of 10 °C. T_i was always in softening stage of coal since values below softening did not affect the fluid characteristics, whereas T_i values above maximum fluidity (T_{mf}) increased the amount of fluid material and the temperature of maximum fluidity, which might reduce coke quality.

In addition, fast heating/quenching tests were performed to ascertain whether the fluid characteristics of the blends could be preserved in a two-stage heating process. The tests comprised of a fast heating stage at 10 °C min^{-1} from 330 °C to T_i followed by fast quenching at 50 °C min^{-1} to room temperature and slow heating of 3 °C min^{-1} to 500 °C. Finally, the effects of biomass torrefaction, amount of sample to make the pellet (1.5 g or 5 g) and particle size of the biomass (<500 μm or >500 μm) were determined under optimum heating conditions.

The micro-strength of semicokes prepared with 5 g of sample and obtained at 600 °C was determined as per the method detailed by Ragan and Marsh [17]. Briefly, two charges of semicoke (2 g, particle sizes 0.60–1.18 mm) were placed into two separate cylinders of 25.4 mm internal diameter and 305 mm length and sealed by steel dust caps. Each cylinder contained 12 steel ball-bearings of 8 mm in diameter. The semicokes were subjected to 200 rotations at a speed of 0.42 Hz to measure three different particle size fractions: >0.6 mm (R_1), 0.6–0.212 mm (R_2) and <0.212 mm (R_3). The R_i indices were obtained from duplicate tests. The micro-strength index (MSI) was obtained by the sum of R_1 and R_2 indices (>0.212 mm).

Thermogravimetric analysis (TGA) tests were carried out on the coals and Scots pine using a TA SDT Q600 instrument. Approximately 45 mg of sample was heated from room temperature to 1100 °C using two different heating regimes. The first regime involved heating the coal or biomass from room temperature to 1100 °C at a rate of 3 °C min^{-1}. In the second set of tests, the samples were heated using two different heating rates. The sample was heated from room temperature to 440 °C (coal A) or 450 °C (coal B) at a rate of 10 °C min^{-1} and then the sample was heated to 1100 °C at the rate of 3 °C min^{-1}. A nitrogen flow rate of 100 cm^3 min^{-1} was used to sweep out the volatile products.

The yields (χ) of coke from coal, char from biomass and coke from the blend were determined using Eqs. (1)–(3) respectively:

$$\chi_{\text{coke}}^{\text{coal}} = \frac{\text{Coke weight at 1100 °C (g)}}{\text{Coal weight at 100 °C (g)}} \tag{1}$$

$$\chi_{\text{char}}^{\text{biomass}} = \frac{\text{Char weight at 1100 °C (g)}}{\text{Biomass weight at 100 °C (g)}} \tag{2}$$

$$\chi_{\text{coke}}^{\text{blend}} = \chi_{\text{coke}}^{\text{coal}} + \chi_{\text{char}}^{\text{biomass}} \tag{3}$$

The residues from TGA were analysed using elemental analysis. The fraction of C (f_C) was measured using a CE Instruments Flash EA 1112 Series elemental analyzer. All measurements were repeated in duplicate and the environmental impact of the addition of biomass was determined using the following equations assuming absence of synergistic effects

Table 2 – Proximate and ultimate analysis of Scots pine (SP).

	Moisture (%)	Ash (% db)	VM (% daf)	Fixed carbon (%)	C (%)	H (%)	N (%)	S (%)	O[a] (%)
SP	16.7	0.8	82.3	14.6	56.5	5.0	0.8	<0.1	37.6

a By difference.

(i.e. blend carbonization behaviour can be predicted from individual components):

$$\text{C emissions from coal (g)} = \left\{W_{\text{coal}}\,(\text{g}) \times f_{\text{C}}^{\text{coal}}\right\} - \left\{W_{\text{coal}}\,(\text{g}) \times \chi_{\text{coke}}^{\text{coal}} \times f_{\text{C}}^{\text{coke}}\right\} \tag{4}$$

$$\text{C emissions from biomass (g)} = \left\{W_{\text{biomass}}\,(\text{g}) \times f_{\text{C}}^{\text{biomass}}\right\} - \left\{W_{\text{biomass}}\,(\text{g}) \times \chi_{\text{char}}^{\text{biomass}} \times f_{\text{C}}^{\text{char}}\right\} \tag{5}$$

$$\begin{aligned}\text{C emissions from blend (g)} &= \left\{W_{\text{coal}}\,(\text{g}) \times f_{\text{C}}^{\text{coal}} + W_{\text{biomass}}\,(\text{g}) \times f_{\text{C}}^{\text{biomass}}\right\} \\ &\quad - \left\{W_{\text{coal}}\,(\text{g}) \times \chi_{\text{coke}}^{\text{coal}} \times f_{\text{C}}^{\text{coke}} + W_{\text{biomass}}\,(\text{g}) \times \chi_{\text{char}}^{\text{biomass}} \times f_{\text{C}}^{\text{char}}\right\}\end{aligned} \tag{6}$$

To calculate the difference in the amount of carbon released from coal in the blend, the following equation was used:

$$\text{C emissions from coal in blend (g)} = W_{\text{coal}}\text{ in blend} \times \left(f_{\text{C}}^{\text{coal}} - \chi_{\text{coke}}^{\text{coal}} \times f_{\text{C}}^{\text{coke}}\right) \tag{7}$$

The values obtained from the equation above are for carbon emitted from equal amounts of starting coal and blend. However, the blend will produce a lower coke yield than the coal. In order to determine the carbon emissions from similar coke yields (C′ emissions), the coke yield ratio for coal and blend must be introduced in Eq. (7):

$$\text{C}'\text{ emissions from coal in blend (g)} = \text{C emissions from coal in blend (g)} \times \frac{\chi_{\text{coke}}^{\text{coal}}}{\chi_{\text{coke}}^{\text{blend}}} \tag{8}$$

Therefore, the reduction of carbon emissions in the coke oven for similar amounts of coke from coal and blend will be given by:

$$\text{Reduction C emissions (\%)} = \left(1 - \frac{\text{C}'\text{ emissions from coal in blend (g)}}{\text{C emissions from coal (g)}}\right) \times 100 \tag{9}$$

3. Results and discussion

3.1. *Standard and fast heating rate conditions in coal and biomass*

Fig. 1 shows the trends for complex viscosity (η^*) and change in plate gap (ΔL) as a function of temperature for the pellets of coals A and B, and the complex viscosity as a function of temperature for the <500 μm and >500 μm particle size fractions of pristine and torrefied Scots pine when using the standard heating rate in coke ovens of 3 °C min^{-1}.

Coal A develops maximum fluidity at 449 °C where the complex viscosity reaches a minimum of around 6.6×10^3 Pa s. Coal B develops less fluidity than coal A and it shows a minimum in complex viscosity of around 1.5×10^5 Pa s at 465 °C. Table 1 shows that higher values of minimum complex viscosity are associated to lower values of Gieseler maximum fluidity (i.e. 534 ddpm for coal A and 48 ddpm for coal B). A comparison of the change in plate gap for both coals indicates that coal A expands and collapses significantly during softening and resolidification as a result of its highly viscous or liquid character whereas the volume of coal B does not undergo any significant changes in the thermoplastic temperature range due to its predominantly elastic or solid character.

All the Scots pine samples show two minima in complex viscosity at around 280 °C and 340 °C that can mainly be ascribed to the degradation of hemicellulose and cellulose respectively [6]. There is also a minimum at 90 °C in the pristine Scots pine that can be ascribed to the presence of water. The results might suggest that the >500 μm fraction develops more fluidity than the fines fraction. However, there are not qualitative differences in the results suggesting that the shift in the complex viscosity trend between the two fractions arises from particle size effects rather than changes in the amount of fluid material. Moreover, a comparison of the pristine and the torrefied Scots pine samples for a given particle size fraction indicates that the complex viscosity values are lower in the torrefied biomass than in the untreated counterpart. This suggests that torrefaction causes an increase in particle size through agglomeration. In order to avoid misleading interpretation of the results by these particle size effects, only the <500 μm fraction of pristine Scots pine will be used in the following tests unless otherwise stated.

Fig. 2 presents the changes in complex viscosity and change in plate gap as a function of temperature for pellets of coal A when using fast heating rates of 10 and 20 °C min^{-1} in the temperature ranges 330–420 °C, 330–430 °C and 330–440 °C. As expected, an increase in heating rate causes a decrease in the minimum complex viscosity reflecting an increase in fluidity. The same effect is caused by an increase in the final temperature for fast heating, i.e. the highest amount of fluid material in the coal is obtained when fast heating is carried out to 440 °C. This is also accompanied by a small increase in the temperature of maximum fluidity (ca. 5 °C). The extents of expansion and collapse of the sample mass, as measured by the changes in plate gap, do not differ to a great extent by altering the heating conditions. This behaviour suggests that the high concentration of fluid material in coal A is able to create pathways and easily diffuse through the sample mass.

Fig. 3 shows the same tests for pellets of coal B, which develops less fluidity than coal A. In this case, only two final temperatures for fast heating were studied (440 °C and 450 °C) as the softening temperature range is smaller than in coal A (15 °C cf. 25 °C). Likewise to coal A, fluidity development increases with the increase in heating rate and the increase in final temperature for fast heating. Simultaneously, the expansion and collapse of the sample mass increase significantly, which can be rationalised by the difficulty of the fluid phase to percolate through the sample mass. This hypothesis suggests that these fast heating conditions could be used to control porosity development in coals that develop minima in complex viscosity of $\geq 10^5$ Pa s.

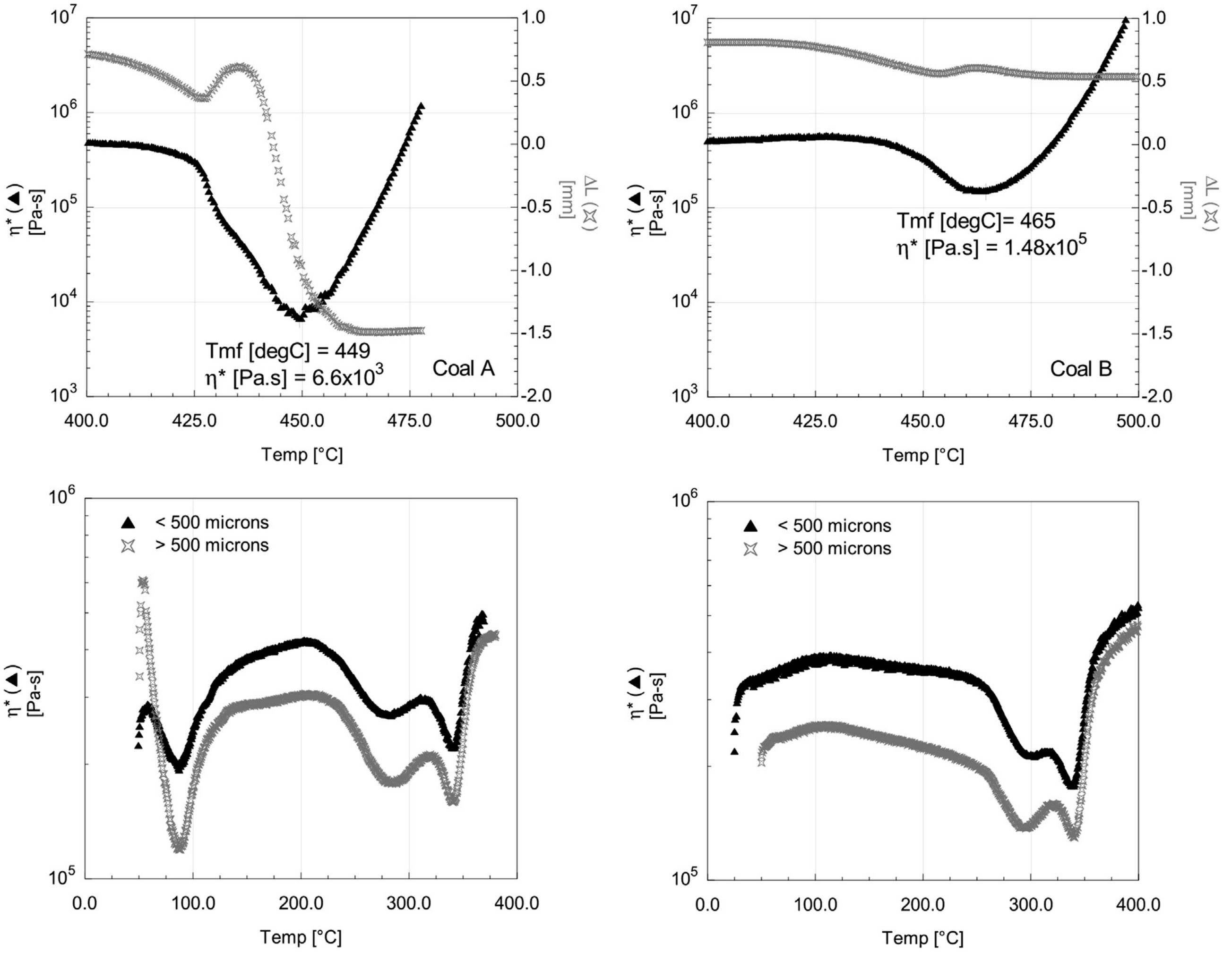

Fig. 1 – Complex viscosity (η^*) and change in plate gap (ΔL) as a function of temperature for coal A (top, left) and coal B (top, right) at 3 °C min^{-1} from 330 °C and complex viscosity as a function of temperature for pristine Scots pine (bottom, left) and torrefied Scots pine (bottom, right) with particle sizes $<$500 μm and $>$500 μm at 3 °C min^{-1}.

The results for both coal A and coal B indicate that there is an optimum heating rate and optimum final temperature for fast heating to maximise the amount of fluid material in the coal without altering the temperature of maximum fluidity. Intuitively, the optimum final temperature for fast heating would be that just below the temperature of maximum fluidity, which is around 440 °C for coal A and 450 °C for coal B. Regarding the heating rate, coals A and B were heated using 3 °C min^{-1}, 6 °C min^{-1}, 10 °C min^{-1} and 20 °C min^{-1} from 330 °C to 440 °C (coal A) and to 450 °C (coal B). As expected, there was an increase in fluidity with the increase in heating rate and the power-law relationship between complex viscosity and heating rate previously reported by Castro Díaz et al. [11] was found, which can be written as follows:

$$\eta^*_{\text{coal}} = C_1 \times (r_\text{h})^{C_2} \tag{10}$$

where η^*_{coal} is the minimum complex viscosity of the coal, r_h is the heating rate, and C_1 and C_2 are constants.

Regarding biomass samples, fast heating rates retained the fluidity of the material at higher temperatures, but the fluid component was not thermally stable over the thermoplastic temperature range of coal and decreased very rapidly, as previously found by Castro Díaz et al. [6]. Hence, biomass will not intuitively increase the overall fluidity in coking blends.

3.2. *Effect of fast heating rate conditions in blends*

Blends consisting of coal A or coal B with a mass fraction of 5% Scots pine were prepared and studied in the rheometer. Initially, the effect of heating rate on the fluidity of the blend was elucidated (Fig. 4). In the case of the blend of coal A with Scots pine, the fluidity of the blend increased when increasing the heating rate from 3 °C min^{-1} to 6 °C min^{-1}, but the viscoelastic properties did not differ with heating rates of 6–20 °C min^{-1}. On the other hand, the increase in fluidity for the blend of coal B and Scots pine increased with heating rate following the order 3 °C min^{-1} $<$ 6 °C min^{-1} to 10 °C min^{-1} $<$ 20 °C min^{-1}. The minima in complex viscosity for coal A and coal B when using the standard heating rate of 3 °C min^{-1} is respectively

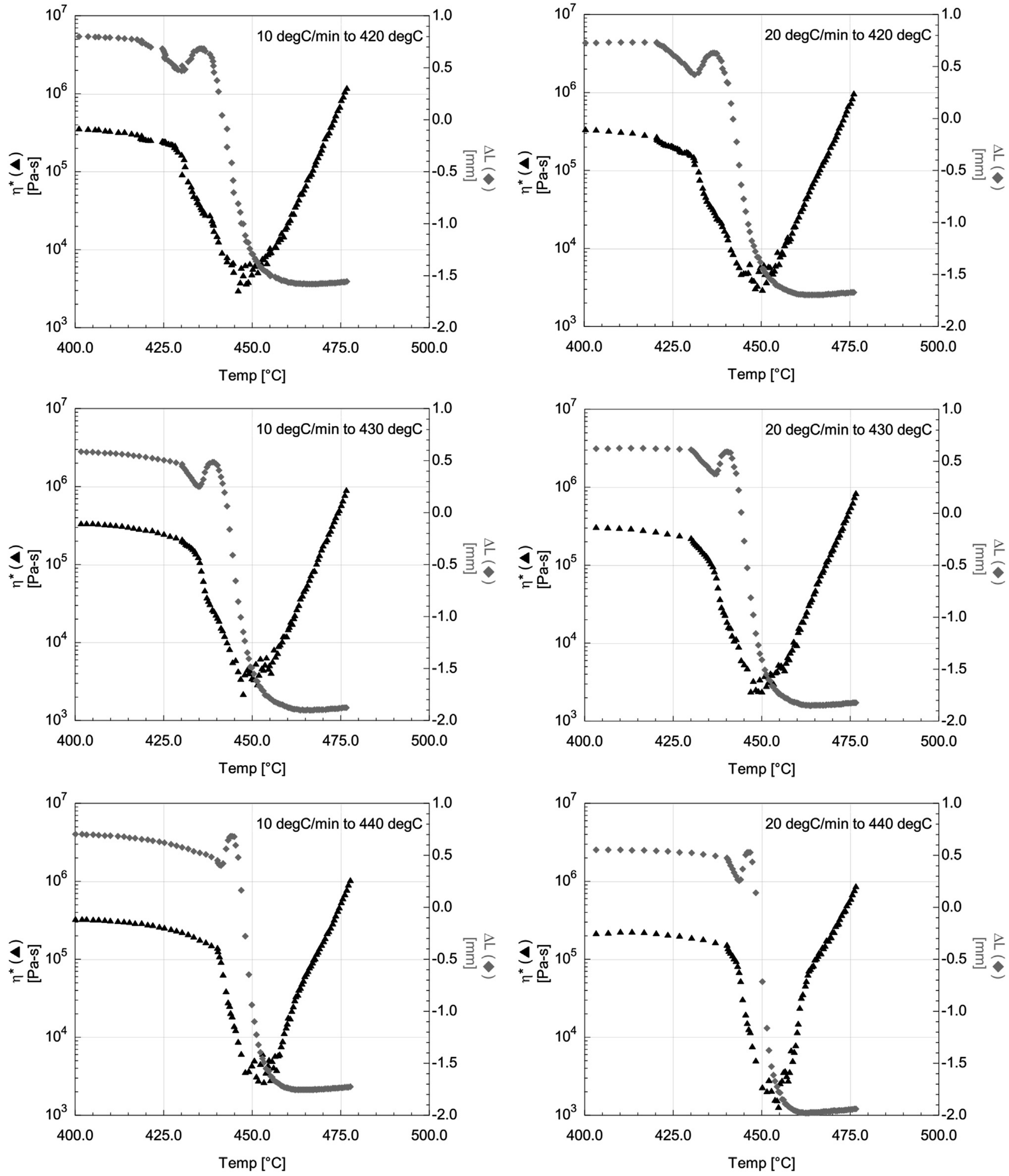

Fig. 2 – Complex viscosity and change in plate gap as a function of temperature for coal A with fast heating of 10 °C min^{-1} and 20 °C min^{-1} to 420 °C, 430 °C and 440 °C.

6.6×10^3 Pa s and 1.5×10^5 Pa s (Fig. 1). Therefore, the use of a heating rate of 10 °C min^{-1} with the blends seems to lead to values of minimum complex viscosity that are comparable to those in the coals alone under standard heating conditions. Furthermore, the same power-law relationship found with the coals alone (Eq. (10)) also applies to these blends.

In other respect, it is important to ascertain how much biomass can be added to coking blends without reducing fluidity development significantly. In this manner, Scots pine was added in concentrations of 5%, 10% and 15% to coal A and the blends were characterised in the rheometer under a heating rate of 10 °C min^{-1} to 440 °C (Fig. 4). An increase in the

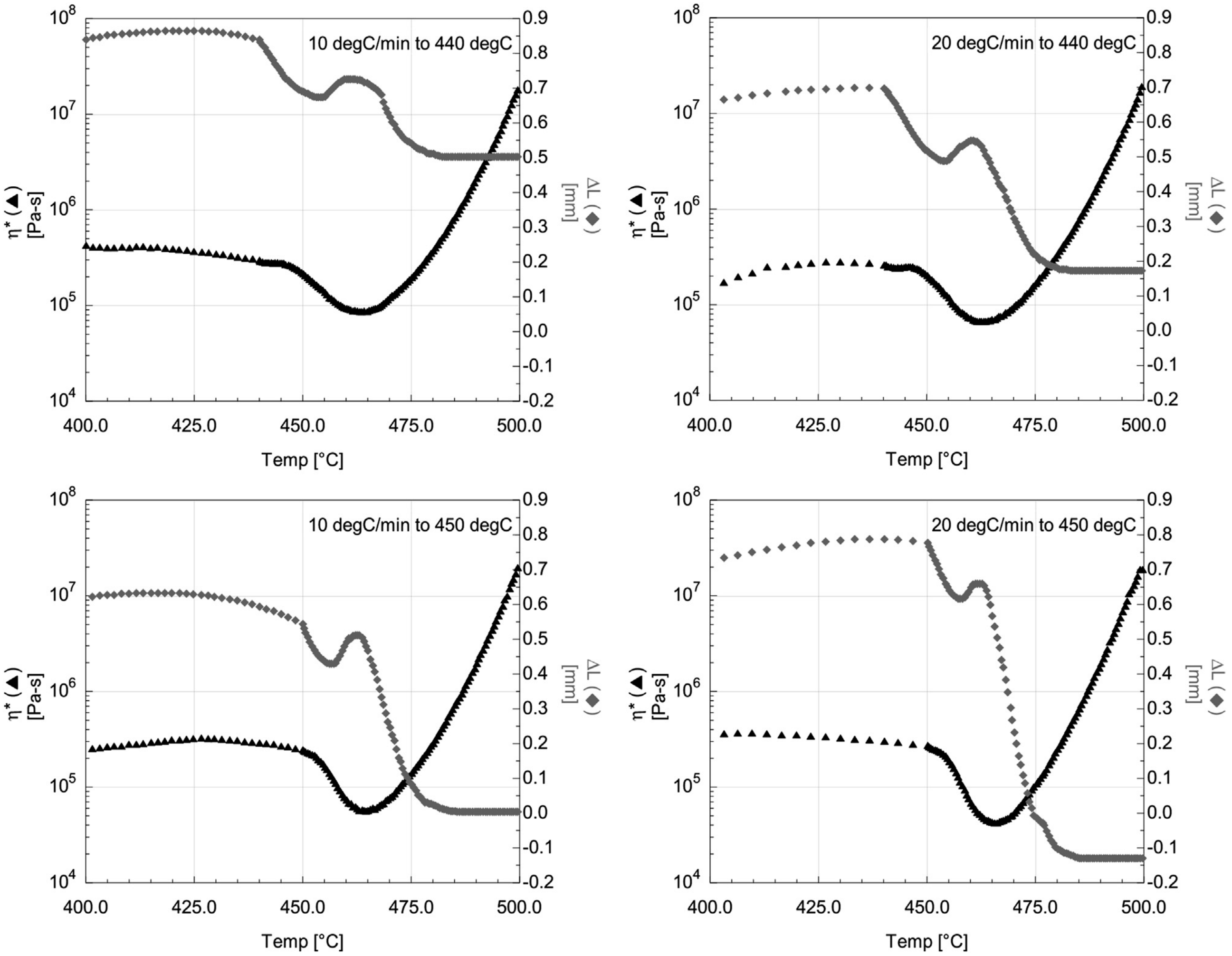

Fig. 3 – Complex viscosity and change in plate gap as a function of temperature for coal B with fast heating of 10 °C min^{-1} and 20 °C min^{-1} to 440 °C and 450 °C.

amount of biomass reduces the fluidity of the blend considerably and an exponential relationship was found between the minimum complex viscosity and the fraction of Scots pine in the blend. This exponential relationship has also been found in binary coal blends [18,19] and it is expressed in the equation below:

$$\eta^*_{\text{blend}} = \eta^*_{\text{coal}} \times \exp(B\varphi_{\text{biomass}}) \tag{11}$$

where η^*_{blend} and η^*_{coal} are respectively the minimum complex viscosity of the blend and coal, ϕ_{biomass} is the fraction of biomass in the blend, and B is an exponential coefficient. Applying the same exponential relationship to blends of coal with miscanthus, pine wood and sugar beet studied by Castro Díaz et al. [6] in previous work, it can be said that B reflects any interactions between the blend components, i.e. an increase in the exponential coefficient is associated to higher interactions and reduction of the fluid phase. Eqs. (10) and (11) can be combined to produce:

$$\eta^*_{\text{blend}} = C_1 \times (r_{\text{h}})^{C_2} \times \exp(B\varphi_{\text{biomass}}) \tag{12}$$

Fig. 5 shows a good correlation between the experimental and calculated complex viscosity values using Eq. (12) for the blends of coal A and Scots pine at 3 °C min^{-1} and 10 °C min^{-1}. The parameter B did not change significantly with heating rate (around 17–21) and it was chosen as 19 for the blend of coal A and Scots pine. C_1 and C_2 were calculated using Eq. (10) for the coal alone and fast heating to 440 °C.

Eq. (12) can be re-arranged to obtain an equation that can predict the heating rate necessary to achieve the optimum minimum complex viscosity for a particular composition of the blend:

$$r_{\text{h}} = \sqrt[C_2]{\frac{\eta^*_{\text{blend}}}{C_1 \times \exp(B\varphi_{\text{biomass}})}} \tag{13}$$

The parameter η^*_{blend} could be substituted with the minimum complex viscosity of the coal alone at standard heating conditions of 3 °C min^{-1}. Nonetheless, additions of >20% biomass to coking blends would impair coke strength and could require heating rates that are unfeasible in commercial coke ovens due to heat transfer limitations.

3.3. *Evaluating pellet and process modifications*

A change in pellet mass may also influence fluidity development as an increase in mass should favour the trapping of the

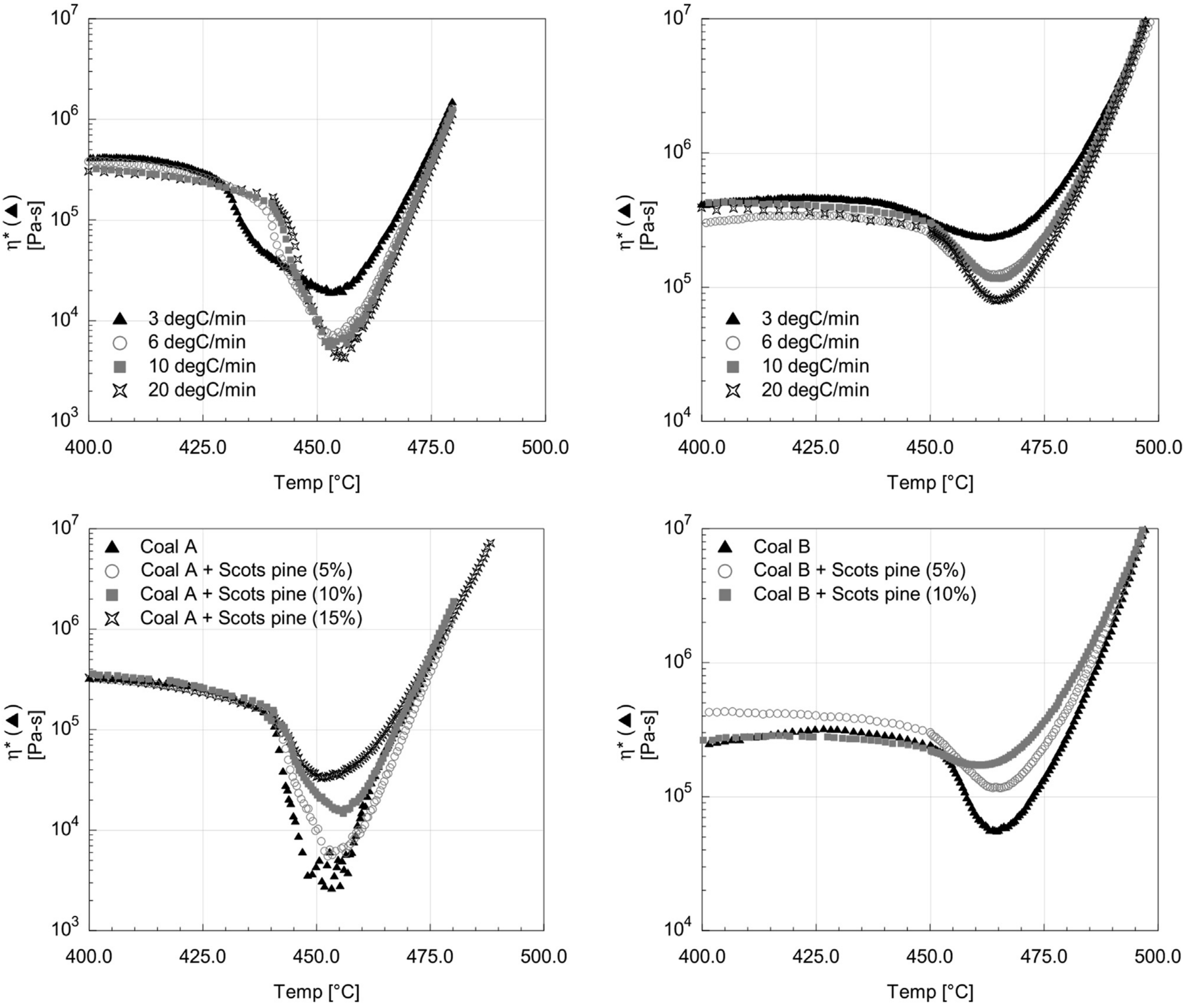

Fig. 4 – Complex viscosity as a function of temperature for the blend of coal A with 5% Scots pine when using different heating rates to 440 °C (top, left), for the blend of coal B with 5% of Scots pine when using different heating rates to 450 °C (top, right), for coal A and blends with Scots pine (up to 15%) when using a heating rate of 10 °C min^{-1} to 440 °C (bottom, left) and for coal B and blends with Scots pine (up to 10%) when using a heating rate of 10 °C min^{-1} to 450 °C (bottom, right).

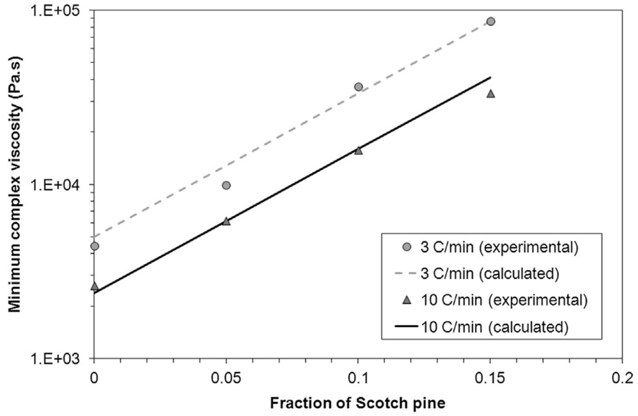

Fig. 5 – Experimental and calculated values of minimum complex viscosity as a function of the fraction of Scots pine in the blends with coal A when using heating rates of 3 °C min^{-1} and 10 °C min^{-1} to 440 °C.

liquid phase, and thus, to cause an increase in fluidity development. As expected, the increase in pellet size from 1.5 g to 5 g in blends of coal B and torrefied Scots pine (>500 μm) caused a decrease in minimum complex viscosity (not shown), but it also increased the temperature of maximum fluidity by around 15 °C, which might affect semicoke strength.

The effect of biomass particle size, biomass torrefaction and blend pre-heating on fluidity development was also studied (Fig. 6). Blends of coal B with a mass fraction of 5% of pristine Scots pine with particle sizes <500 μm and >500 μm and using a fast heating rate of 10 °C min^{-1} were used to study the effect of particle size; torrefaction effects were elucidated on blends of coals A and B with 5% Scots pine (<500 μm); and the same blends were pre-heated at 10 °C min^{-1} and quenched at 50 °C min^{-1} before carrying out slow heating tests at 3 °C min^{-1}.

Fig. 6 proves that an increase in the particle size does not affect the fluid characteristics although the extent of collapse in

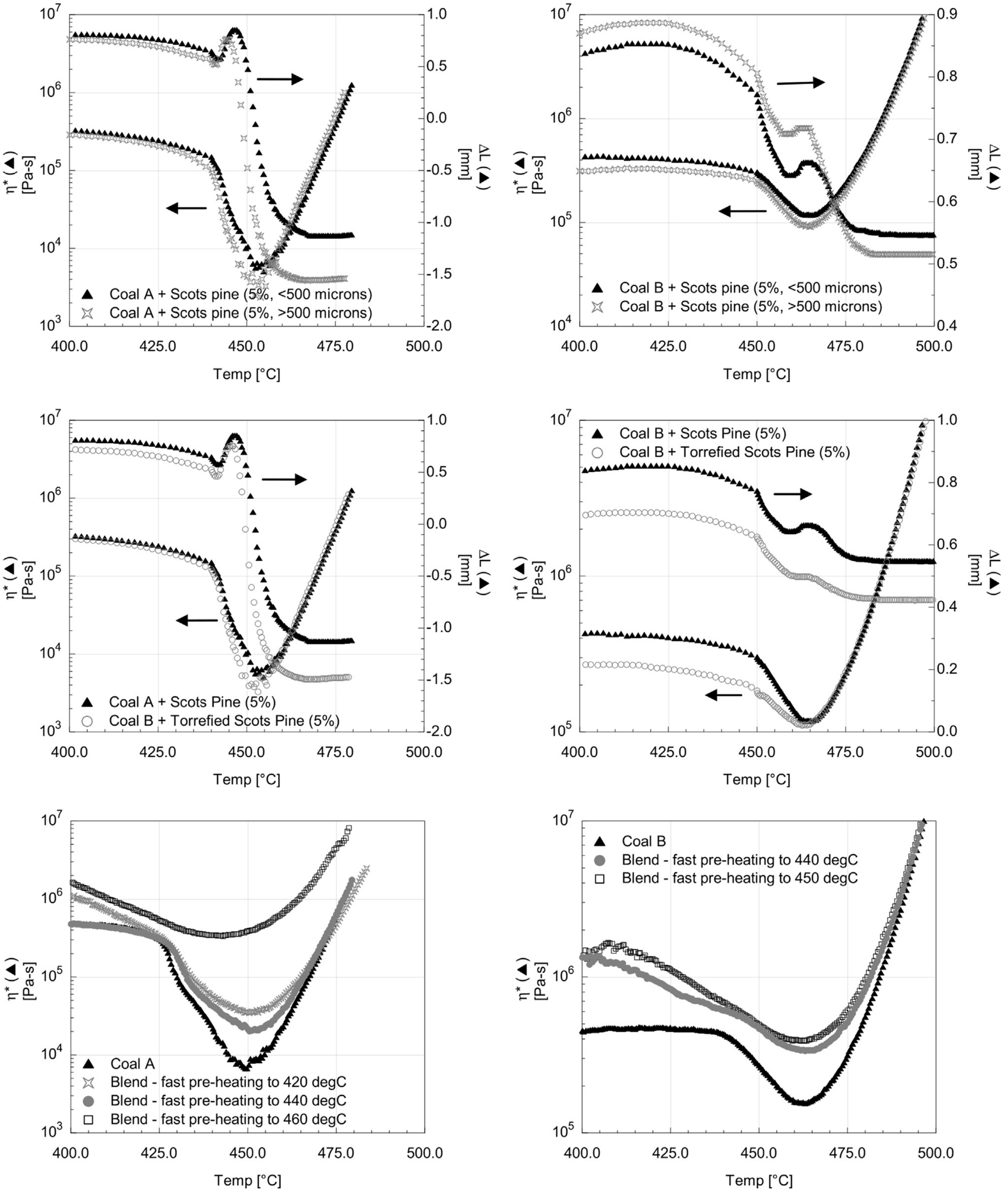

Fig. 6 – Effect of particle size (top), biomass torrefaction (middle) and blend pre-heating (bottom) on fluidity development and mass expansion/collapse.

the blend containing Scots pine with particle sizes >500 μm is higher than in the blend with fines. Neither torrefaction causes significant differences in the amount of fluid material evolving from the blend. Therefore, torrefied biomass could be used in coking blends to increase the bulk density and coke yield of the blend without causing any deleterious effect on fluidity. Pre-heating the blend destroys fluidity development to such an extent that it contains less fluidity than the coal alone under

Table 3 – Percentage of particle size fractions (R_1, R_2, R_3) and micro-strength index (MSI) values of the semicokes at 600 °C.

Coal B (%)	Scots pine > 500 μm (%)	Heating conditions	R_1	R_2	R_3	MSI
100	0	3 °C min^{-1}	15.8	48.9	35.3	64.7
90	10	10 °C min^{-1} to 450 °C	22.7	42.5	34.8	65.2
90	10	20 °C min^{-1} to 450 °C	20.9	41.9	37.2	62.8

Particle size fractions: R_1 (>0.6 mm); R_2 (0.6–0.212 mm); R_3 (<0.212 mm); MSI (>0.212 mm).

slow heating. Moreover, the amount of fluid material in the blend depends on the final temperature for fast heating, whereby fluidity development in blends of coal A decreases when pre-heating is carried out to 440 °C > 420 °C ≫ 460 °C. In the case of coal B, pre-heating the blends to 440 °C or 450 °C causes a similar reduction in fluidity that is also lower than the fluidity in the coal alone at 3 °C min^{-1}. On the whole, pre-heating the blend prior charging in the coke oven is not a viable alternative to preserve fluidity development.

3.4. *Effect of fast heating on semicoke strength*

Table 3 presents the micro-strength values determined with the method detailed by Ragan and Marsh [17] for the semicokes obtained at 600 °C from coal B and the blends with a mass fraction of 10% Scots pine.

The blend with 10% Scots pine and fast heating of 10 °C min^{-1} possesses higher strength than the coal alone and slow heating (3 °C min^{-1}), as reflected by the higher micro-strength index. It is also important to note that both blends have higher R_1 values (>0.6 mm fraction) than the coal with slow heating. The strength for the blend under a heating rate of 10 °C min^{-1} could be directly attributable to the increase in fluidity development in the coal under these conditions, which in turn, increases the cohesion between coal and biomass particles. However, an increase in heating rate in the blend from 10 °C min^{-1} to 20 °C min^{-1} seems to reduce the semicoke strength despite the expected increase in fluidity development. A possible explanation is that the further increase in heating rate promotes pore coalescence that results in a weaker structure. However, further investigation would be necessary to confirm this hypothesis.

Overall, fast heating rates of 10 °C min^{-1} could potentially be used as an alternative methodology to preserve fluidity development and coke strength in blends of biomass with coking coals having medium volatile matter contents (ca. 25% daf). However, it is not possible to achieve these heating rates in industrial coke ovens due to heat transfer limitations, and hence, additional heating systems must be introduced to produce semicokes from the coal and biomass blends using this methodology. These semicokes could then be charged to the coke oven as long as they possess low reactivity to carbon dioxide (CRI) and high resistance to abrasion besides high strength in order to produce high quality coke after carbonization. Moreover, the pellet size and particle sizes of coal and biomass must be optimized since the pellets studied in this work are not realistic for industrial application.

3.5. *Reduction in non-renewable carbon emissions*

Table 4 lists the coke/char yields obtained at 1100 °C obtained from TGA and carbon contents of the residues obtained from elemental analysis for the coal and Scots pine samples. The results indicate that fast heating conditions increase the coke and char yields by approximately 1–2%, and that biomass torrefaction increases the char yield of the biomass (8%). An increase in biomass particle size reduces the char yield by 2–4%, which could be caused by density effects or compositional differences between the two size fractions.

These values were used to calculate the amount of carbon released from single coals, biomass and blends when using fast heating conditions. This was then used to obtain the change in the amount of non-renewable carbon released into the atmosphere by the blends, since the carbon released from the blends is the contribution of both non-renewable carbon from coal and renewable carbon from biomass. The carbon released from biomass is considered to be renewable because it can be reabsorbed into the carbon cycle. Table 5 presents the values calculated using Eqs. (1)–(9) for the carbon emissions from the coals, Scots pine (<500 μm) and blends with a mass fraction of 10% Scots pine assuming that the amount of starting material is 100 g.

Table 4 – Coke/char yields from coals and Scots pine and carbon contents of the residues obtained at 1100 °C.

Sample and heating conditions	Coke/char yield	C content (%)
SP (<500 μm), 3 °C min^{-1} to 1100 °C	20	82.02
SP (<500 μm), 10 °C min^{-1} to 450 °C, 3 °C min^{-1} to 1100 °C	21	84.84
Torrefied SP (<500 μm), 10 °C min^{-1} to 450 °C, 3 °C min^{-1} to 1100 °C	29	86.61
SP (>500 μm), 3 °C min^{-1} to 1100 °C	18	89.63
SP (>500 μm), 10 °C min^{-1} to 450 °C, 3 °C min^{-1} to 1100 °C	17	91.50
Coal A, 3 °C min^{-1} to 1100 °C	70	87.20
Coal A, 10 °C min^{-1} to 450 °C, 3 °C min^{-1} to 1100 °C	72	89.10
Coal B, 3 °C min^{-1} to 1100 °C	75	83.77
Coal B, 10 °C min^{-1} to 450 °C, 3 °C min^{-1} to 1100 °C	76	85.94

Table 5 – Calculated values for carbon emissions from coals, Scots pine and blends with 10 wt% Scots pine when using fast heating of 10 °C min^{-1}.

	Coal A	Coal B	SP < 500 μm	Coal A (90%) + SP (10%)	Coal B (90%) + SP (10%)
Sample weight (g)	100	100	100	100	100
C fraction (f_C)	0.786	0.791	0.565	0.764	0.768
Amount of C (g)	78.6	79.1	56.5	76.4	76.8
Coke or char weight (g)	72.0	76.0	21.0	66.9	70.5
C fraction in coke/char	0.891	0.859	0.848	0.887	0.858
Amount of C in coke/char (g)	64.2	65.3	17.8	59.3	60.5
Total C emissions (g)	14.4	13.8	38.7	17.1	16.3
C emissions from coal (g)	14.4	13.8	n.a.	13.0	12.4
C′ emissions from coal (g)	14.4	13.8	n.a.	14.0	13.4
Reduction C emissions (%)	0	0	n.a.	3.1	3.0

n.a.: not applicable.

Coal A alone releases 14.4 g of carbon for every 100 g of coal utilized, whilst the blend with 10% Scots pine increases this value to 17.1 g due to the high volatile matter content of the biomass (ca. 80%, Table 2). The same effect is shown by coal B where 13.8 g of carbon is released when the coal is used alone and this value increases to 16.3 g when blended with 10% Scots pine. However, the contribution of coal to carbon emissions (non-renewable carbon) is reduced from 14.4 to 13.0 g in the case of coal A, and from 13.8 to 12.4 g for coal B. If the data are normalized to take into account similar coke yields rather than similar amounts of starting material, the emission of non-renewable carbon is increased from 13.0 g to 14.0 g for coal A and from 12.4 g to 13.4 g for coal B, which represents a reduction of around 3% in non-renewable carbon emissions for both coals.

Although this value is relatively low, the micro strength results in Table 3 suggest that up to 15% of Scots pine could be added to coal B without adversely affecting the strength of the resultant coke. If this is the case, the amount of non-renewable carbon released into the atmosphere could be decreased by 5%. A further reduction in carbon emissions could be achieved by reducing the volatile matter content of the biomass in order to maximise the final coke yield. This could be accomplished by optimizing the selection of the biomass, carrying out biomass torrefaction, or introducing small amounts in the blend of high char yield biomass derived products such as charcoal (<5%).

4. Conclusions

1. Relatively fast heating rates (up to 20 °C min^{-1}) improve the fluid characteristics of coking blends with biomass. Although an increase in the concentration of biomass in the blend is detrimental for fluidity development, an increase in heating rate favours the formation of fluid material. The relationships identified with these two parameters and the minimum complex viscosity of the coal and blends have been used to develop an equation that can predict the required heating rate to attain optimum fluid properties for a blend with specific biomass concentration.
2. Increasing the biomass particle size or using torrefied biomass had little effect on the amount of fluid material evolving in the blend during carbonization, Increase in the pellet mass favours the retention of the fluid material in the blend but preheating the blend to the softening temperature range of coal prior coke oven charging destroys the fluidity of the blend.
3. The semicoke of a blend of a medium volatile (25% daf) coking coal with 10% Scots pine using fast heating of 10 °C min^{-1} presented good strength, confirming that this approach could be considered for commercial coking blends with biomass. However, heating rates of 10 °C min^{-1} are not feasible in existing coke ovens due to heat transfer limitations. A possible solution to counter this drawback could be the use of an additional pre-heating systems (e.g. conveyor belt oven).
4. The addition of 10% Scots pine resulted in a significant 3% reduction in non-renewable carbon emissions, which could be improved by increasing the char yield of the biomass (e.g. torrefaction).

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